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Melt composition and heat treatment at growth of $Gd_2Si_2O_7$ — based crystals

Ia.V.Gerasymov, O.Ts.Sidletskiy, V.N.Baumer, S.V.Neicheva*

Institute for Scintillation Materials, STC "Institute for Single Crystals", National Academy of Sciences of Ukraine, 60 Lenin Ave., 61001 Kharkiv, Ukraine
*State Scientific Institution "Institute for Single Crystals", National Academy of Sciences of Ukraine, 60 Lenin Ave., 61001 Kharkiv, Ukraine

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Paper is devoted to obtaining of scintillation crystals based on gadolinium pyrosilicate $Gd_2Si_2O_7$. Basic problems of crystal growth and ways of their solving are discussed. Crystals obtained by optimized procedure shows very high efficiency at registration of X-rays.

Получены сцинтилляционные кристаллы на основе пиросиликата гадолиния $Gd_2Si_2O_7$ (GPS). Обсуждаются основные проблемы, связанные с получением данного материала, а также предлагаются варианты их решения. Кристаллы выращенные с учетом оптимизации процедуры роста демонстрируют высокую эффективность регистрации рентгеновского излучения.

1. Introduction

Inorganic scintillation materials are crucial element of modern detecting systems in high energy physics, environmental and nuclear monitoring, medicine, oil well logging. Ce-doped rare earth silicates are among the most efficient and durable materials for these applications. In particular, lutetium oxyorthosilicate Lu_2SiO_5:Ce (LSO:Ce) [1, 2] is a material of choice for most of modern positron emission tomography (PET) devices [3,4].

Besides the oxyorthosilicate phase, RE_2O_3–SiO_2 (RE — rare earth element), there is a compound with molar ratio RE_2O_3–$2SiO_2$ and common formulae $RE_2Si_2O_7$ called RE pyrosilicate or disilicate. It was reasonable to check scintillation efficiency of this class of compounds at Ce-doping. Good scintillation efficiency and light yield ~26000 phot/MeV was demonstrated with lutetium pyrosilicate, $Lu_2Si_2O_7$:Ce [5, 6]. At the same time, Ce-doped yttrium pyrosilicate $Y_2Si_2O_7$:Ce demonstrates low-to-moderate scintillation efficiency [7, 8]. The important factor is that Lu, as well as Er, Yb disilicates are only congruent melting compounds among lanthanide disilicates. $Gd_2Si_2O_7$:Ce (GPS:Ce) showed very promising scintillation characteristics at monitoring of γ-rays and thermal neutrons [9]. The latter becomes possible due to very large thermal neutron capture cross section by the ^{155}Gd and ^{157}Gd isotopes [10]. The valuable factor is that GPS melting temperature is significantly lower than in orthosilicates and LPS. This matters at minimization of crystal production cost, in particular, it prolongs Ir crucible lifetime. Gadolinium oxide cost is by order of magnitude lower compared to Lu_2O_3 of the same purity.

Therefore GPS:Ce has big potential as scintillation materal. The main obstacle at implementation of this advantage is connected to complex obtaining procedure of GPS:Ce single crystals due to incongruent melting [11]. This work deals with search for appropriate growth methods and procedures of GPS crystal growth.

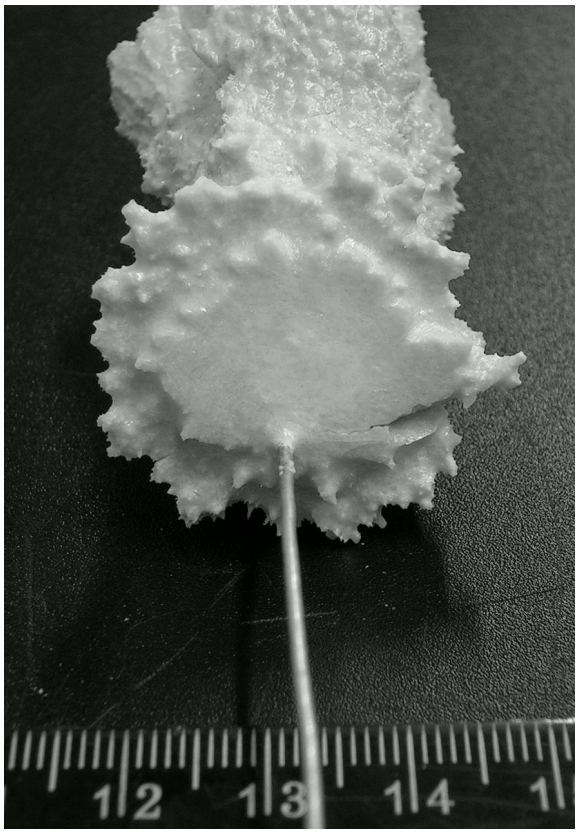

Fig. 1. Ingot obtained without heat-treatment of the melt.

2. Experimental procedure

Starting oxides Gd_2O_3(4N), SiO_2(5N), CeO_2(4N), La_2O_3(4N), Pr_6O_{11}(4N), Sc_2O_3(4N) were mixed in stoichiometric ratio, then they were calcined at 1700°C in inert atmosphere during 10 h for pyrosilicate phase synthesis [12].

Crystal growth was performed in Ar atmosphere in conventional induction heating furnace using Ir crucible with diameter 60 mm and height 60 mm by Czochralski and Top Seeded Solution Growth (TSSG) methods. Growth rate and rotation rate in Czochralski method were 1–1.2 mm/h and 15–30 rot/min respectively. Growth and rotation rates in TSSG methods were 0.3–0.5 mm/h and 5–10 rot/min, respectively. Ir wire with the diameter 1 mm was used as a seed. GPS:Ce crystals with diameter up to 30 and length up to 50 mm were obtained by Czochralski method. By TSSG method the samples of nominally undoped, Ce-doped, and La–Ce, Sc–Ce and La–Pr co-doped gadolinium pyrosilicates were obtained by this procedure.

Fragments of the crystals was studied using the X-ray automated single crystal diffractometer "Xcalibur-3" (Oxford Diffraction Ltd.) equipped with "Sapphire-3" CCD-detector and graphite monochromator.

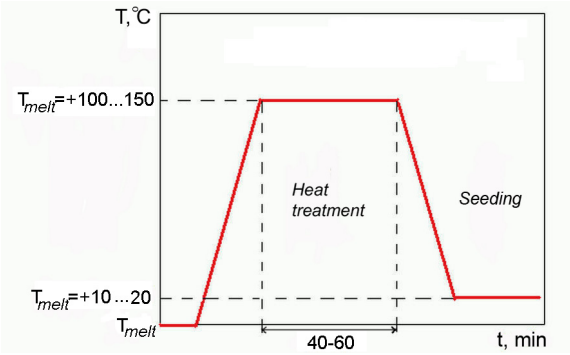

Fig. 2. A sketch of heat treatment procedure.

Luminescence spectra was determined with a combined fluorescent lifetime and steady-state spectrometer FLS 920 (Edinburgh Instruments) on samples with dimensions 3×3×3 mm^3 and 1×1×1 m^3. X-ray luminescence was measured at excitation by X-ray tube with copper cathode (40 mkA, 40 kV).

3. Results and discussion

3.1. Crystal growth

It was shown [13] that at heavy Ce doping (~10 at. %), peritectic point at phase diagram moves closer to the GPS stoichiometric composition. It means a possibility to obtain single crystals directly from melt. However, in several growth experiments only ingots containing mix of $Gd_2Si_2O_7$, $Ce_2Si_2O_7$, $Gd_{4.66}Si_3O_{13}$, SiO_2 phases were obtained (Fig. 1). Phase analysis of crystallized melt showed its inhomogeneity. For better melt homogenization, a procedure of melt heat treatment before seeding was utilized (Fig. 2).

GPS:Ce crystal was obtained by Czochralski method after the heat treatment of the melt is shown on Fig. 3a.

The proposed procedure appears to be appropriate also at growth of co-doped GPS crystals by Top Seeded Solution Growth method with SiO_2 self flux with SiO_2 excess up to 4 mol. %. This method was utilized to grow GPS; GPS:10 at. % Ce; GPS:5 at. % Sc, 0.2 at. % Ce; GPS:10 at. % La, 1 at. % Ce; GPS:10 at. % La, 0.2 at. % Pr (Fig. 3b).

It is known [11, 14] that 7 types of polymorph modifications are inherent to RE pyrosilicates, which are denoted by letters from A to G. Undoped GPS may exist only

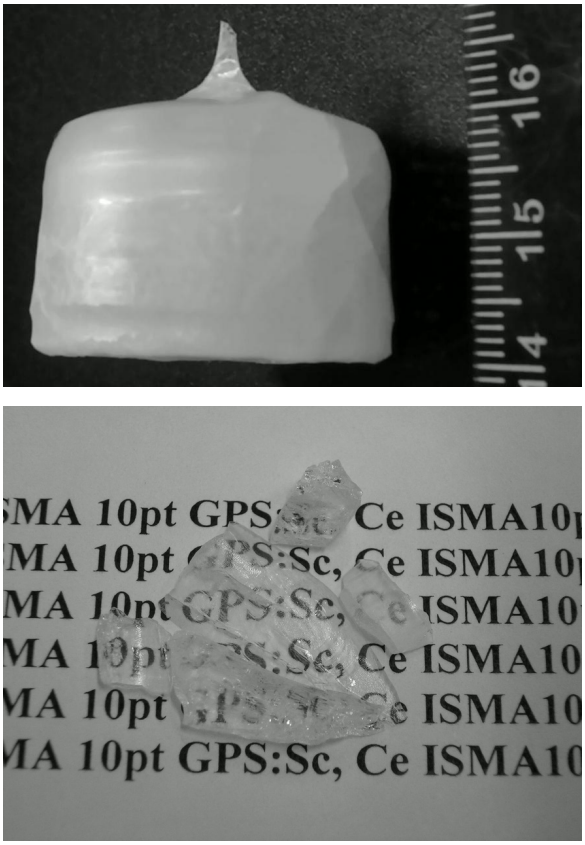

Fig. 3. a — GPS:Ce obtained by Czochralski method, b — GPS:Sc, Ce obtained by TSSG method.

in two types of polymorph modifications: orthorhombic E type and triclinic B type. In our experiments, obtained crystals correspond to the orthorhombic E, triclinic F, and tetragonal A modifications (Table). Formation of non-characteristic structures for GPS is linked to variation of both averaged rare-earth cation radius and melting temperature at codoping, and temperature conditions of crystallization. For crystals grown by TSSG the structure changes from orthorhombic E to triclinic F and tetragonal A type as averaged RE cation radius increases.

The following formulae was used for calculation of the averaged RE cation radius [15]:

$$R_{REEav}=\sum\left(R_i\cdot\frac{C_i}{\sum_1^n C_i}\right), \quad (1)$$

where R_{REEav} is the averaged RE cation radius, R_i — ionic radii of RE elements contained in crystal, C_i — molar concentrations of RE elements.

R_{REEav} values are shown in the third column in Table. The fourth column shows the cations, which ionic radii correspond to these R_{REEav} and polymorph types they may form. One can see that obtained structures are in agreement with literature data [14].

Orthorhombic E type GPS crystals were obtained by TSSG method from the melt with the following composition: GPS; GPS:5 at. % Sc, 0.2 at. % Ce, and by Czochralski method from the melt with composition GPS:10 at. % Ce. The value of R_{REEav} for scandium activated crystals is 0.928 Å (Table). This value is close to the cation radius of the trivalent terbium, and E structure is inherent to $Tb_2Si_2O_7$ [14]. R_{REEav} in GPS:10 at. % Ce is about 0.946 Å (Table) and equals to the Eu^{3+} ionic radius. In its turn, $Eu_2Si_2O_7$ may exist in the four structural types (A, B, E, F) [14]. The value of R_{REEav} of crystalline sample of GPS co-activated with lanthanum and praseodymium is 0.947 Å (Table) . This value also matches the Eu^{3+} ionic radius. This sample belongs to the F structural type with triclinic structure. GPS:10 at. % La, 1 at. % Ce belongs to the tetragonal structural type A and its averaged radius is also close to Eu^{3+}. Low-temperature modification of $Eu_2Si_2O_7$ has the same type of structure. Apparently, a crystal structure type A can

Table. Structure modifications of obtained crystals. Comments are in text.

Raw material composition	Type of structure	R_{REEav}	Possible types of structure	Growth method
GPS:5 at. % Sc, 0.2 at. % Ce	**E**	0.928 Å	Tb^{3+} (B,**E**)	TSSG
GPS	**E**	0.938 Å	Gd^{3+} (B,**E**)	TSSG
GPS:10 at. % Ce	**E**	0.946 Å	Eu^{3+} (A,B,**E**,F)	Cz
GPS:10 at. % Ce	**F**	0.946 Å	Eu^{3+} (A,B,E,**F**)	TSSG
GPS:10 at. % La, 0.2 at. % Pr	**F**	0.947 Å	Eu^{3+} (A,B,E,**F**)	TSSG
GPS:10 at. % La, 1 at. % Ce	**A**	0.948 Å	Eu^{3+} (**A**,B,E,F)	TSSG

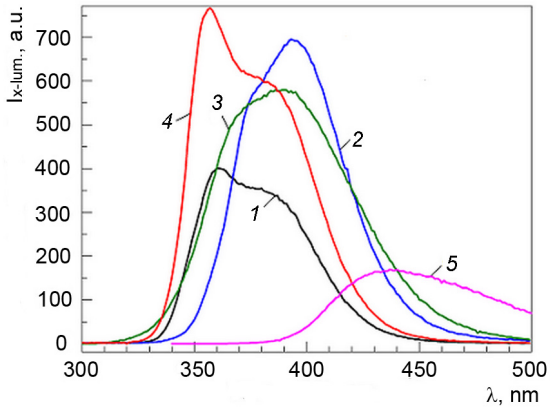

Fig. 4. X-ray luminescence spectra:
1 — GPS:10 at. % Ce (orthorhomb.),
2 — GPS:10 at. % Ce (tricl.),
3 — GPS:10 at. % La, 1 at. % Ce (tetragon.),
4 — GPS:5 at. % Sc, 0.2 at. % Ce (orthorhomb.),
5 — GSO:Ce.

be synthesized directly due to decrease of crystallization temperature in TSSG method or following the polymorphic transition from B type to the type A, but not due to polymorphic transitions E–A or F–A, because these transitions are not allowed [14]. Therefore, difference in structures of crystals with 10 at. % Ce obtained from melt with the same composition by Czochralski and TSSG is called by difference in crystallization temperatures.

3.2. Characterization of crystals

To evaluate the performance of obtained crystals, their luminosity under X-ray excitation has been checked (Fig. 4). The most intense X-ray luminescence is observed in GPS:Sc,Ce crystal (3.3× relatively to GSO:Ce). The observed luminescence bands are clearly related to $5d$–$4f$ radiative transitions in Ce^{3+} ion.

The same Ce^{3+} luminescence band is also appears in nominally undoped and Pr^{3+}-doped crystals (Fig. 5). Obviously, this is attributed to uncontrolled admixtures in the starting oxides and/or contamination at the stages of raw material synthesis and crystal growth. No remarkable d–f luminescence in Pr^{3+} has been registered at room temperature under X-rays. At the same time, f–f luminescence bands of Pr^{3+} near 500 and 600 nm are weak compared to Ce^{3+} band at 325–425 nm and Gd^{3+} narrow peak at 313 nm.

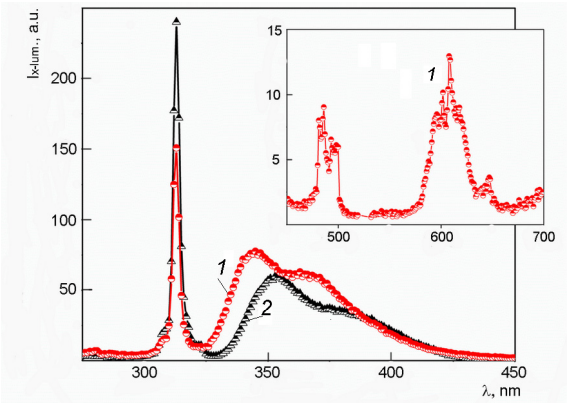

Fig. 5. X-ray luminescence spectra: *1* — GPS: La, Pr, *2* — GPS pure (comments are in text).

4. Conclusions

The developed melt heat treatment method provides obtaining of bulk single crystalline GPS-based crystals by Czochralski and TSSG method. XRD data show that heat treatment improves the melt homogeneity that results in elimination of foreign phase inclusions in crystals. The observed luminosities show a high efficiency of this class of scintillator materials at registration of ionizing radiation.

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Склад та температурна обробка розплаву при вирощуванні кристалів на основі $Gd_2Si_2O_7$

Я.В.Герасимов, О.Ц.Сідлецький, В.М.Баумер, С.В.Нейчева

Одержано сцинтиляційні кристали на основі піросилікату гадолінію $Gd_2Si_2O_7$. Обговорюються основні проблеми, пов'язані з отриманням даного матеріалу, а також пропонуються варіанти їх рішення. Кристали, які вирощено з урахуванням оптимізації процедури росту, демонструють високу ефективність реєстрації рентгенівського випромінювання.